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(21) International Application Number: PCT/GB92/00820 (22) International Filing Date: 6 May 1992 (06.05.92) (30) Priority data: 9109928.3 8 May 1991 (08.05.91) GB (71) Applicant (for all designated States except US): SOLVAY INTEROX LIMITED [GB/GB]; Baronet Works, Baronet Road, Warrington, Cheshire WA4 6HB (GB). (72) Inventors; and (75) Inventors/Applicants (for US only) : KAGERMEIER, Sonja [DE/DE]; Noestrasse 10, D-8000 Munich 71 (DE). REVELL, Christopher [GB/GB]; 28 Wilmot Avenue, Great Sankey, Warrington, Cheshire WA5 3BJ (GB). WILSON, Sharon, Lesley [GB/GB]; 14 Ridgebourne Close, Callands, Warrington, Cheshire WA5 5YB (GB).	(74) Agent: PEARCE, Timothy; Solvay Interlox, Patent Dept., Moorfield Road, Widnes, Cheshire WA8 0JU (GB). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent), US. Published <i>With international search report.</i>	
(54) Title: THICKENED COMPOSITIONS (57) Abstract <p>Many aqueous compositions containing a peroxygen compound have a very low viscosity and thus easily run off non-horizontal surfaces. Particularly when the peroxygen compound is a soluble peracid, the compositions are difficult to thicken successfully, because many commonly available thickening systems for aqueous media either fail to thicken them or are decomposed and/or decompose the peroxygen compound substantially during storage. The compositions, preferably containing a soluble peracid are thickened with an alkali metal silicate, preferably sodium silicate, such as $\text{Na}_2\text{O} \cdot (\text{SiO}_2)_2$, suitably in an amount of from about 2 to 6 % of the composition and normally introduced in the form of a concentrated aqueous composition. The compositions may contain additionally an alkylammonium methosulphate. Preferred peracid solutions include dilute equilibrated peracetic acid solutions. The solutions when thickened to form a viscous liquid are suitable for disinfecting hard surfaces and when thickened to form a gel are suitable for suspension in an aqueous medium, for example in block form.</p>		

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Thickened Compositions

10 The present invention relates to thickened compositions and particularly to thickened peroxygen compositions.

 During recent years, increasing attention has been paid by industry and the general public in Western Europe and North America to the environmental effects of the many
15 substances that are employed in modern life. One of the classes of substances which have hitherto been widely employed comprises chlorine and oxychlorine derivatives thereof. Such compounds have been reported to generate under appropriate circumstances carcinogenic compounds and
20 as a result, industry is seeking alternatives or replacements for such compounds in order to allay any residual public anxiety.

 An alternative class of compounds comprises peroxygen compounds, of which one sub-class of especial interest
25 comprises peracids which contain the moiety $-CO-OOH$. Peracids like hydrogen peroxide enjoy the substantial advantage of generating oxygen, either as such or in an active form during its deployment rather than chlorine or active chlorine species upon which environmentalists
30 currently cast doubts. Furthermore, for a range of purposes such as disinfection, oxidation and bleaching, many of which are encountered domestically, peracids are more effective in general than hydrogen peroxide.

 A number of the peracids are either liquid themselves or
35 are produced conveniently in aqueous solution. Although such compositions are particularly appropriate for the treatment of or incorporation in liquid media, they are less appropriate for the treatment of solid surfaces, and

particularly non-horizontal surfaces on account of the ability of liquid compositions to flow away from the point of contact. In consequence, and in order to extend the range of applications for peracids, it would be desirable to
5 devise peracid-containing compositions that flowed less freely.

In principle, liquid compositions can be rendered less free-flowing by the incorporation of materials which thicken the liquid or introduce structure into the liquid. However,
10 it is not impractical to expect that substances which have hitherto been effective thickeners for other liquids would automatically to be suitable for thickening liquid peracids or peracid solutions. This difficulty derives from the very same properties of the peracids that make them
15 effective oxidising agents and bleaches. Interaction with thickeners during storage can result in the mutual decomposition of the peracid and the thickener, which in turn not only negates the beneficial effects of thickening, but also progressively removes the capability of the peracid
20 to perform its desired task. It will be recognised that the problem is especially apparent in the case of peracids which are themselves either liquid or are present in solution. There is also a second important difficulty in attempting to thicken peracid solutions. The presence of
25 the peracid and the corresponding carboxylic acid from which it can be derived, tends to significantly inhibit thickening. It is believed that the difficulty arises from interference of the peracid and/or carboxylic acid with aqueous structuring mechanisms which enable surfactants and
30 like materials to thicken aqueous solutions. However, it will be understood that the instant invention does not depend upon the accuracy of the foregoing belief or explanation, but instead it relies upon the results actually demonstrated.

35 By comparison with soluble peracids, the problem can be somewhat diminished in the case of substantially insoluble solid peracids that are suspended in particulate form in aqueous media, because the peracid and the liquid constitute

different physical phases that consequently minimise the extent of chemical interaction between them, and the thickening of the aqueous phase can occur with a lessened risk of interference from dissolved peracid species.

5 It will be understood that some other potential thickeners may initially or after a brief period of storage produce a much thickened composition, but one which is rather unstable, in that its viscosity falls away rapidly from its peak. Tests employing anionic polyacrylamides
10 fell into that category.

It is an object of the present invention to seek to identify thickening substances which are capable of thickening peroxygen compositions. It is a second object of some preferred embodiments to identify materials capable of
15 thickening soluble peracid compositions and obtain thereby compositions which are relatively stable during storage. It is a third object of a further set of embodiments of the present invention to identify materials which can thicken peroxygen compositions to produce viscous compositions which
20 can be applied for disinfecting and/or cleansing purposes to non-horizontal surfaces.

According to the present invention there are provided aqueous compositions comprising a peroxygen compound at least partly in solution together with a thickener
25 characterised in that the thickener comprises an alkali metal silicate in an amount sufficient to increase the viscosity to at least 100cPs.

By the use of a thickening system of the present invention it is possible to obtain solutions which are
30 thickened and in which the peroxygen compound decomposes by not more than an acceptable extent during storage. In other words, the composition enjoys both physical and chemical stability.

The invention thickening system is intended particularly
35 for thickening soluble peracids. However, it will be recognised that the thickening system may alternatively be employed to thicken alternative peroxygen compositions, including compositions which are easier to thicken than

soluble peracid compositions. In many embodiments, the peroxygen compound is organic. Thus, for example, the system is applicable to organic peroxides, ie organic compounds containing a -C-O-O-H or C-O-O-C- moiety, including alkyl, cycloalkyl or aryl peroxides, acyl peroxides, peroxy carbonates, and organic hydroperoxides and to compositions containing less or even poorly soluble peroxyacids such as those containing at least 8 carbons.

In particular, though, the system is applied to compositions containing soluble peracids, which may include low molecular weight aliphatic peroxyacids, for example containing up to 6 carbon atoms, of which especially preferred examples comprise peracetic acid and perpropionic acid. Other examples include perbutyric acid, persuccinic acid and perglutaric acid. The compositions may alternatively include soluble aromatic peroxyacids, such as monoperphthalic acid, or sulphoperbenzoic acid. A mixture of peracids may be employed, if desired.

The peroxygen compound, such as the peracid, may be present in a wide range of concentrations, for example up to about 40%. For any component, % herein is by weight based on the total weight of the composition, unless specifically stated otherwise. The lower limit is at the discretion of the user, but is normally not below about 0.1%. The invention is particularly applicable to ready to use compositions containing a low concentration of active peroxygen compound, and for example compositions intended for application for cleansing and/or disinfecting purposes to hard surfaces and particularly to non-horizontal surfaces. Such dilute compositions typically contain from 0.25 to about 5% by weight of an organic peroxygen compound, preferably a peracid, for example peracetic acid and in a number of practical embodiments the peroxygen compound content will be from about 0.5 to 2%. It will be recognised that such compositions may contain a significant concentration of hydrogen peroxide, which may, for example, comprise from about 1 to 12% of the composition, and in a number of embodiments from 3 to 10%.

The peracid compositions, and particularly those containing aliphatic peracids are often conveniently derived by oxidation of the corresponding aliphatic carboxylic acid with aqueous hydrogen peroxide, and will often contain residual amounts of both the carboxylic acid and hydrogen peroxide. Thus, the compositions may contain up to 40% of the corresponding carboxylic acid and up to 40 % hydrogen peroxide, with a minimum water content usually of 20%. However, in dilute peracid solutions, the concentration of the carboxylic acid and of hydrogen peroxide each tend to be selected in the range from about 1 to 12%. The total concentration of carboxylic acid plus percarboxylic acid is often from 3 to 20% and in many instances from 3 to 15%. It is often convenient to restrict the concentration of hydrogen peroxide to no greater than 7%. In many preferred compositions, equilibrium amounts of carboxylic acid, percarboxylic acid and hydrogen peroxide are present.

The thickening system of the present invention comprises an alkali metal silicate. The amount of silicate to employ depends on how thick a composition is desired. By appropriate adjustment of the silicate concentration, it is possible to obtain a wide range of compositions. At one extreme, the compositions remain easily pourable, but distinctly more viscous than the corresponding composition without added silicate. At the other extreme, the compositions are gelled, forming a product that is in effect a solid. The silicate concentrations tend to be selected in the region of at least 2% by weight in order to obtain compositions having viscosities of about 300cPs or higher and in many embodiments the concentration is not greater than 6% by weight.

The silicate is usually sodium silicate, on account of its widespread availability at a reasonable cost, but other silicates such as potassium or lithium may be employed instead of all or part of the sodium silicate.

Alkali metal silicates are usually represented by the formula $(M_2O) \cdot (SiO_2)_m$ in which M represents an alkali metal and m the mole ratio of alkali metal oxide, eg soda to

silica. Silicates are obtainable in the range of m = about 1 to about 4. Particularly effective results have been obtained in the region of m = 2. It will be recognised that the viscosity of the composition is to some extent
5 dependent upon the mole ratio of alkali metal oxide to silica. For introduction of the same concentration of alkali metal silicates, there is a tendency for the viscosity to decrease as the mole ratio m increases.

It is desirable to select relatively pure alkali metal
10 silicates and particularly samples which are not contaminated with an excessive residue of transition metals. By so doing, it is possible to maintain peroxygen compound stability. For example, when thickening peracid compositions, it has been found desirable to use a silicate
15 that has been supplied as or purified to an iron content of not greater than about 20ppm. Naturally, though, if it is anticipated that contaminating metal ions may be present that would promote peroxygen compound decomposition, it is desirable to incorporate one or more chelating stabilisers,
20 such as are described subsequently herein.

The silicates are conveniently introduced into the composition in the form of an aqueous solution, preferably concentrated and for example containing between about 30 and 50% by weight alkali metal silicate, in order to assist even
25 distribution and mixing of the silicate with the peroxygen compound solution. Direct introduction of solid silicate is not recommended.

The physical state of the composition may also be modified by the presence of one or more viscosity modifiers.
30 By so doing, it is possible to fine tune, to at least some extent, the ability of the composition to be poured.

The pH of the composition is a further factor affecting the viscosity attained by a thickened composition during storage and the rate at which thickening occurs in the
35 present invention. In particular, it is desirable to employ a pH of at least 1, approximately, so as to encourage thickening to occur and in practice the pH is normally not higher than about 4.5. As a generalised expression of a

trend, thickening becomes progressively quicker and easier to obtain as the pH of the solution is higher. A preferred pH range for the compositions comprise from about pH 3 to 4.5. Advantageously, many compositions such as dilute
5 peracetic acid compositions attain that range without any further adjustment.

It will be understood that the thickened compositions of the present invention tend to thicken over a period of time, rather than attain the maximum thickness quickly.
10 Advantageously, this means that the compositions normally still be readily handled using conventional bottling or liquid transporting equipment for a reasonable period after introduction of the thickening system.

The compositions may include one or more stabilisers for
15 peracids and/or hydrogen peroxide so as to encourage the chemical stability of the thickened products. Known stabilisers for peroxy compounds include aminopolycarboxylic acids, such as EDTA and DTPA, or N-heterocyclic aromatic carboxylic acids such as quinolinic acid, picolinic acid and
20 dipicolinic acid. Particularly effective stabilisers comprise organic polyphosphonic acids, including hydroxyethylidene-diphosphonic acid and aminopolymethylene phosphonic acids. The latter often satisfy the general formula:

25 $X_2N-(-CHR-CHR-NX-)_n-NX_2$ in which X represents $-CH_2-PO_3H_2$
R represents H or the two R substituents combine to complete a cyclohexane ring, and n is an integer from 1 to 3.
Examples of the formula include ethylenediaminetetra-
(methylene phosphonic acid), diethylenetriaminepenta-
30 (methylene phosphonic acid) and cyclohexanediaminetetra-
(methylene phosphonic acid).

In addition to the foregoing components, the composition may also contain one or more surfactants, for example amine oxides, and additionally or alternatively, one or more
35 perfumes and/or dyes, preferably selected at least partly on the basis of resistance to oxidation.

The compositions of the present invention can be made by introducing the selected amount of the alkali metal

silicate, preferably in concentrated aqueous solution, into an aqueous precursor composition containing essentially water and the peroxygen compound, such as an aqueous solution of peracid, which solution can optionally contain
5 any residual amounts of the corresponding carboxylic acid and hydrogen peroxide, and agitating the resultant mixture to distribute the thickener substantially evenly through the mixture. The silicate solution introduced preferably has a concentration of at least 30% w/w up to a saturated
10 solution.

Desirably, the pH of the solution is measured and adjusted, if necessary, by introduction of the appropriate choice from a mineral acid if the solution is insufficiently acid or an alkali if the solution is too acid. The process
15 can be conducted at any convenient temperature, for example at the prevailing ambient temperature which is typically in the range of from 10 to 35°C. Alternatively, the mixture may be gently heated to not higher than about 50°C so as to encourage rapid distribution of the thickener and the
20 mixture thereafter permitted to cool to ambient.

Some of the compositions of the present invention, and particularly those having a viscosity in the region of about 200 to 600cPs are intended for application domestically to surfaces, such as non-horizontal surfaces, which it is
25 desired to disinfect and clean, thereby taking advantage of the disinfectant properties of the peroxygen compound, especially the peracid and the cleansing properties of the detergents. The peroxygen compositions in solid form may be incorporated in particulate or granular washing or
30 disinfecting compositions or dispersed in blocks or bars. Such blocks or bars may also incorporate substances such as waxes, either natural or synthetic polymers or very poorly soluble aliphatic carboxylic acids or poorly soluble derivatives and/or mixtures thereof which can regulate and
35 retard the extent of contact between the peroxygen compound composition and for example a liquid medium such as flushing toilet water.

Accordingly, a second aspect of the present invention comprises the use the aforementioned invention compositions for disinfecting and cleansing by applying the composition to a hard surface and permitting contact to be maintained
5 until at least some disinfection has occurred.

The invention compositions may be applied using conventional means and will also take into account the physical state of the composition, particularly whether it is a viscous pourable liquid or a gel. Thus, in its
10 simplest, the compositions may be poured or smeared onto a distributor such as a cloth or sponge and applied to a receiving surface by passage of distributor across the surface. Alternatively, the compositions which have a sufficiently low viscosity for them to be pourable, may be
15 forced through a distributing nozzle directly onto the receiving surface, for example by squeezing a resilient deformable storage container. Compositions in gel form may be applied by a spatula or like article or as indicated previously by incorporation in a host composition or block.

20 The surfaces onto which the compositions may be applied are often domestic and especially in the kitchen and other locations in which micro-organisms may be found. Suitable receptive surfaces are usually made from wood, glass, ceramics, plastic laminates and metal, and include work
25 surfaces, sinks, pipework, walls, floors, and especially toilet bowls. It will be recognised, though, that similar potentially infected surfaces may be found in non-domestic situations, such as in commercial kitchens, food processing apparatus or containers or brewery or distillery vessels or
30 hospitals or in animal or poultry-rearing establishments or in glass houses or other areas where the maintenance of hygienic conditions is important. The present invention includes the use of invention compositions in such non-domestic situations.

35 The compositions may subsequently be removed from the surfaces by water washing, possibly applied using a cloth, sponge or like article.

A further use for a gelled composition is to form it into a block and suspend it, either as such or within a permeable container, within a liquid medium that it is desired to disinfect, such as process water, industrial circulating water or domestically the water supply to a toilet.

Having described the invention in general terms, specific embodiments thereof will now be described in greater detail by way of example only.

For use in the Examples, a batch of silicate solution was made dissolving sodium silicate powder having an $\text{SiO}_2:\text{Na}_2\text{O}$ mole ratio of 2:1, obtainable from Joseph Crossfield under their trade name Crystal C Powder to a concentration of 40%. The solution contained on analysis <10ppm Fe.

Example 1

In this Example, a thickened peracid composition was made by stirring at laboratory ambient temperature (about 22°C), the aforementioned silicate solution (5g) and hydroxyethylidene-diphosphonic acid available under the Trademark DEQUEST grade 2010 (100ppm) into a solution of peracetic acid available from Interlox Chemicals (100g) which analysed as peracetic acid (1%) acetic acid (9%) hydrogen peroxide (6%) and the balance water. The resultant composition had a pH of about 3.5, which fell to about pH 3.3 during storage. After 16 weeks, the composition had a viscosity measured using a Brookfield synchroelectric viscometer of 400cPs. The available oxygen (Avox) of the composition was measured on production and after 16 weeks storage at 22°C using a conventional ceric sulphate/sodium thiosulphate technique. By comparing the two analyses, it was found that the composition had retained 69% of its Avox.

Example 2

In this Example, Example 1 was repeated, but employing 7g of the sodium silicate solution. The resultant composition had a pH of 3.5 rising to pH 4 after storage for 20 days and a viscosity of about 1500 cPs after 12 days. The composition had become solidified during storage for 20

weeks at 22°C, by which time it had retained 86% of its Avox.

Example 3

In this Example, Example 1 was repeated, but employing
5 13g of the sodium silicate solution. The resultant
composition had a pH of 3.9 rising to pH 4.0 after storage
for 20 days and a viscosity of over 80,000cPs after 16
weeks. The composition retained 47% of its Avox after 16
weeks storage at 22°C.

10 Example 4

In this Example, Example 4 was repeated, but employing
in addition concentrated sulphuric acid, 1.2ml. The
resultant composition had a pH of 1.2, and a viscosity of
about 1400 cPs after 16 weeks. The composition retained 74%
15 of its Avox after 16 weeks storage at 22°C.

Example 5

In this Example, Example 3 was repeated, additionally
incorporating an alkylammonium methosulphate (2g) available
from Stepan under their trademark STEPANQUAT F. The
20 resultant composition had a viscosity of 22,000 cPs after 16
weeks storage at 22°C and had retained 99% of its Avox.

Example 6

In this Example, Example 3 was repeated, additionally
incorporating an amine oxide (2g). After 16 weeks storage
25 at 22°C, the composition had a viscosity of 3000 cPs and had
retained 72% of its Avox.

CLAIMS:-

1. Aqueous compositions comprising a peroxygen compound at least partly in solution together with a thickener characterised in that the thickener comprises an alkali metal silicate in an amount sufficient to increase the viscosity to at least 100cPs.
2. A thickened composition according to claim 1 characterised in that the peroxygen compound is a peracid.
3. A thickened composition according to claim 2 characterised in that the peracid is soluble.
4. A thickened composition according to claim 3 characterised in that the peracid is peracetic acid.
5. A thickened composition according to any preceding claim characterised in that it contains from 0.25 to 5% w/w peracid.
6. A thickened composition according to any preceding claim characterised in that it contains amounts of a carboxylic acid and hydrogen peroxide each selected in the range of from about 1 to 12% w/w.
7. A thickened composition according to claim 6 characterised in that the combined proportions of peracid and carboxylic acid is in the range of from 3 to 15%.
8. A thickened composition according to any preceding claim characterised in that the alkali metal silicate has the formula $(M_2O) \cdot (SiO_2)_m$ in which m is about 2.
9. A thickened composition according to any preceding claim characterised in that the amount of alkali metal

silicate employed is selected in the range of from 2 to 6% w/w of the composition.


10. A thickened composition according to any preceding claim characterised in that the alkali metal silicate is sodium silicate.
11. A thickened composition according to any preceding claim characterised in that the silicate employed has an impurity content of no greater than 20ppm iron calculated as Fe.
12. A thickened composition according to any preceding claim characterised in that the composition after thickening has a pH in the range of from pH3 to pH 4.5.
13. A thickened composition according to any preceding claim characterised in that sufficient alkali metal silicate is employed to attain a viscosity after storage of from about 250 to 600 cPs.
14. A thickened composition according to any of claims 1 to 12 characterised in that sufficient alkali metal silicate is employed to solidify the composition.
15. A thickened composition according to any preceding claim characterised in that it contains additionally an alkylammonium methosulphate.
16. A thickened composition according to any preceding claim characterised in that it contains a stabiliser for peroxygen compounds.
17. A process for preparing a thickened composition by introducing an effective amount of an alkali metal silicate into an aqueous composition containing a peroxygen compound and agitating the mixture.

18. A process according to claim 17 characterised in that the alkali metal silicate is introduced in the form of a concentrated aqueous solution, preferably from 30% w/w to a saturated solution.
19. A process according to claim 17 or 18 characterised in that it employs one or more of the characterising features of claims 2 to 16.
20. Use of a thickened peroxygen composition according to any of claims 1 to 16 or produced by the process of claim 17, 18 or 19 as a disinfectant.
21. A thickened peroxygen composition or a process for making a thickened peroxygen composition or the use of a thickened composition as a disinfectant substantially as described herein with respect to any novel feature or novel combination of features.

INTERNATIONAL SEARCH REPORT

International Application No

PCT/GB 92/00820

I. CLASSIFICATION OF SUBJECT MATTER (if several classification symbols apply, indicate all) ⁶		
According to International Patent Classification (IPC) or to both National Classification and IPC		
Int.Cl. 5 A61L2/18; A01N37/16; A01N59/16		
II. FIELDS SEARCHED		
Minimum Documentation Searched ⁷		
Classification System	Classification Symbols	
Int.Cl. 5	A61L ; A01N	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched ⁸		
III. DOCUMENTS CONSIDERED TO BE RELEVANT⁹		
Category ¹⁰	Citation of Document, ¹¹ with indication, where appropriate, of the relevant passages ¹²	Relevant to Claim No. ¹³
X,P	EP,A,0 429 124 (THE PROCTER AND GAMBLE COMPANY) 29 May 1991 see page 3, line 10 - line 28; claims ---	1-19
X	EP,A,0 167 375 (THE CLOROX COMPANY) 8 January 1986 see claims 1-4 ---	1-19
A	EP,A,0 283 791 (DEGUSSA AKTIENGESELLSCHAFT) 28 September 1988 see claims; examples ---	1-21
A	US,A,4 800 036 (G. ROSE) 24 January 1989 ---	
<p>¹⁰ Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&" document member of the same patent family</p>		
IV. CERTIFICATION		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
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ANNEX TO THE INTERNATIONAL SEARCH REPORT
ON INTERNATIONAL PATENT APPLICATION NO. GB 9200820
SA 58976

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